Supplementary Information

Highly Stereoselective Cyclopropanation of Olefins Catalyzed by a Novel C₃-Symmetric Arsine

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Table of Contents

1. General Experimental Conditions.....	S2
2. General procedure for cyclopropanation reactions.....	S2-S4

1. General Experimental Conditions

Commercially available reagents were used without further purification other than those detailed below. Toluene was distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane and CH₃CN were distilled over calcium hydride. Acetone was distilled from anhydrous CaSO₄. All reactions were performed under a nitrogen atmosphere unless otherwise noted.

Melting points are uncorrected. Melting points were determined on WRS-1 digital melting-point apparatus made by Shanghai Physical Instrument Factory (SPOIF), NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer. The chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications.

2. General Procedure for Preparing *cis*-3-aryl-2-benzoyl-cyclopropane-1,1-dicarbonitriles **3**

The general process for synthesis of *cis*-3-aryl-2-benzoyl-cyclopropane-1,1-dicarbonitriles **3a** - **3j** was as follows: A mixture of **1** (0.167 g, 0.15 mmol), phenacyl bromide (0.238 g, 1.2 mmol), olefin **2** (1 mmol) and NaHCO₃ (0.240 g, 3 mmol) was stirred in CH₃CN at 80 °C. The progress of reaction was monitored by TLC. After completion, water was added and the product was extracted with ethyl acetate. The organic layer was separated, dried over anhydrous sodium sulphate and the solvent evaporated under reduced pressure to afford the crude product, which was subjected to column chromatography over silica gel using hexane/ethyl acetate as eluent to obtain pure product. All products were known and characterized by comparison of their physical and spectroscopic data with those already reported.

Data

3a: *cis*-2-benzoyl-3-phenylcyclopropane-1,1-dicarbonitrile. mp: 130 - 131 °C; lit.^[1] mp: 132 - 133 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.08 - 8.11 (d, 2H), 7.68 - 7.74 (t, 1H), 7.53 - 7.59 (t, 2H), 7.34 - 7.46 (m, 5H), 4.05 (d, 1H, J = 8.0 Hz), 3.91 (d, 1H, J = 8.0 Hz).

3b: *cis*-2-benzoyl-3-(4-nitrophenyl)cyclopropane-1,1-dicarbonitrile. mp: 186 - 187 °C; lit.^[1] mp: 188 - 189 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.14 (d, 2H, J = 8.4 Hz), 8.13 (d, 2H, J = 8.0 Hz), 7.75 - 7.81 (t, 2H), 7.60 - 7.67 (m, 3H), 4.04 (d, 1H, J = 8.0 Hz), 3.92 (d, 1H, J = 8.0 Hz).

3c: *cis*-2-benzoyl-3-(4-fluorophenyl)cyclopropane-1,1-dicarbonitrile. mp: 158 - 159 °C; lit.^[1] mp: 156 - 157 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.11 - 8.13 (d, 2H), 7.72 - 7.78 (t, 1H), 7.50 - 7.64 (t, 2H), 7.37 - 7.41 (q, 2H), 7.14 - 7.19 (t, 2H), 4.00 (d, 1H, J = 8.0 Hz), 3.90 (d, 1H, J = 8.0 Hz).

3d: *cis*-2-benzoyl-3-(4-chlorophenyl)cyclopropane-1,1-dicarbonitrile. mp: 181 - 182 °C; lit.^[1] mp: 180 - 181 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.08 - 8.10 (d, 2H), 7.71 - 7.76 (t, 1H), 7.58 - 7.62 (t, 2H), 7.43 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.7 Hz), 4.01 (d, 1H, J = 8.0 Hz), 3.89 (d, 1H, J = 8.0 Hz).

3e: *cis*-2-benzoyl-3-(4-bromophenyl)cyclopropane-1,1-dicarbonitrile. mp: 166 - 167 °C; lit.^[1] mp: 164 - 165 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.10 - 8.12 (d, 2H), 7.73 - 7.78 (t, 1H), 7.59 - 7.63 (t, d, 4H, J = 8.6 Hz), 7.28 (d, 2H, J = 9.0 Hz), 4.00 (d, 1H, J = 8.0 Hz), 3.87 (d, 1H, J = 8.0 Hz).

3f: *cis*-2-benzoyl-3-(2-chlorophenyl)cyclopropane-1,1-dicarbonitrile. mp: 152 - 153 °C; lit.^[1] mp: 154 - 155 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.76 - 7.78 (m, 2H), 7.52 - 7.63 (m, 4H), 7.26 - 7.42 (m, 3H), 4.04 (d, 1H, J = 8.0 Hz), 3.95 (d, 1H, J = 8.2 Hz).

3g: *cis*-2-benzoyl-3-(2,4-dichlorophenyl)cyclopropane-1,1-dicarbonitrile. mp: 146 -147 °C;

lit.^[1] mp: 144 - 145 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.12 - 8.15 (d, 2H), 7.75 - 7.80 (t, 1H), 7.60 - 7.67 (m, 2H), 7.34 - 7.37 (d, 1H), 7.21 - 7.27 (t, 2H), 3.99 (d, 1H, *J* = 8.2 Hz), 3.92 (d, 1H, *J* = 8.2 Hz).

3h: *cis*-2-benzoyl-3-(4-methylphenyl)cyclopropane-1,1-dicarbonitrile. mp: 157 - 158 °C; lit.^[1]

mp: 156 - 157 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.09 - 8.13 (d, 2H), 7.72 - 7.77 (t, 1H), 7.58 - 7.63 (t, 2H), 7.26 (s, 4H), 4.03 (d, 1H, *J* = 8.0 Hz), 3.86 (d, 1H, *J* = 8.0 Hz), 2.39 (s, 3H).

3i: *cis*-2-benzoyl-3-(3,4-methylenedioxyphenyl)cyclopropane-1,1-dicarbonitrile. mp 187 -

188 °C; lit.^[1] mp: 188 - 189 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.09 - 8.12 (m, 2H), 7.71 - 7.73 (t, 1H), 7.56 - 7.62 (t, 2H), 6.83 - 6.85 (t, 2H), 6.00 (s, 2H), 3.97 (d, 1H, *J* = 8.0 Hz), 3.83 (d, 1H, *J* = 8.0 Hz).

3j: *cis*-2-benzoyl-3-(4-methoxyphenyl)cyclopropane-1,1-dicarbonitrile. mp: 165 - 166 °C; lit.^[1]

mp: 163 - 164 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.08 - 8.11 (d, 2H), 7.71 - 7.76 (t, 1H), 7.58 - 7.63 (t, 2H), 7.31 (d, 2H, *J* = 8.7 Hz), 6.98 (d, 2H, *J* = 8.6 Hz), 3.99 (d, 1H, *J* = 8.0 Hz), 3.86 (d, 1H, *J* = 8.0 Hz), 3.84 (s, 3H).

References

(1) Ren, Z. J.; Cao, W. G.; Ding, W. Y.; Wang, Y.; Wang, L. L. Stereoselective Synthesis of *cis*-1-Aryl-2-benzoyl-3,3-dicyanocyclopropanes in the Presence of KF·2H₂O. *Syn. Comm.* **2004**, *34*, 3785-3792.